



# Hybrid catalysts for the selective catalytic reduction of NO by NH<sub>3</sub>: The influence of component separation on the performance of hybrid systems

Mariam Salazar<sup>a,1</sup>, Stefanie Hoffmann<sup>a</sup>, Olga P. Tkachenko<sup>b</sup>, Ralf Becker<sup>c</sup>, Wolfgang Grünert<sup>a,\*</sup>

<sup>a</sup> Lehrstuhl für Technische Chemie, Ruhr-Universität Bochum, D-44780 Bochum, Germany

<sup>b</sup> N. D. Zelinsky Institute of Organic Chemistry, Russian Academy of Sciences, Moscow, Russia

<sup>c</sup> Huntsman Pigments and Additives, 47829 Krefeld, Germany

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## ABSTRACT

The selective catalytic reduction (SCR) of NO by NH<sub>3</sub> was investigated over physical mixtures of an oxidation catalyst with an SCR catalyst ("hybrid catalyst") in which the components were arranged in variable distance to each other: pressed in mixed particles after grinding the mixture, mixing particles of individual components, and in two-layer and four-layer beds. Using Fe-ZSM-5 or V<sub>2</sub>O<sub>5</sub>-WO<sub>3</sub>/TiO<sub>2</sub> as SCR components and Mn<sub>2</sub>O<sub>3</sub>, Mn-Cu and Ce-Zr mixed oxides as oxidation components, it was observed that the pronounced synergies described in literature are observed only when the components are mixed within the particles. The synergy is strongly attenuated in beds of component particles and fades away completely in the layered structures. This observation is at variance with earlier ideas according to which the oxidation component catalyses the formation of NO<sub>2</sub> which opens a fast SCR reaction path over the SCR component. Instead, a more labile critical intermediate is more likely, e.g., HNO<sub>2</sub>, which may be formed over the oxidation component and proceeds to the SCR sites for further reaction along routes discussed in recent literature. The new understanding is in accordance with earlier observations that correlation between NO oxidation activities of oxidation components and performance of the resulting hybrids was observed to be coarse and to include remarkable outliers.

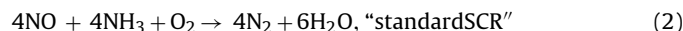
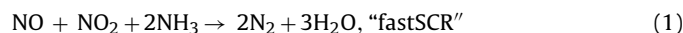
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## 1. Introduction

Although the selective catalytic reduction of NO by NH<sub>3</sub> is a mature technology for purification of flue gases from stationary sources and is presently being commercialized at large scales in exhaust gas treatment of Diesel vehicles [1], research dedicated to the creation of ever more active, selective and stable catalysts remains to be important and attractive. While the installations in cars employ metal-exchanged zeolites (Cu, Fe) or promoted VO<sub>x</sub>-TiO<sub>2</sub> catalysts depending on the application, there has been much effort to present alternative options based, for instance on supported or bulk mixed Mn or Ce oxides [2]. However, Mn-based catalysts tend to release undesired side products (N<sub>2</sub>O) and to suf-

fer from deactivation. Ce-based catalysts often fail to perform well at low temperatures, where significant conversion is needed due to the low exhaust temperatures of modern Diesel engines.

The disclosure of catalyst combinations by Stakheev et al. [3] has recently opened a novel, productive route in this development. These "hybrid" systems combine an oxidation catalyst with an SCR catalyst (up to now Fe zeolites) in mechanical mixtures, which results in much higher activities than the SCR component would achieve alone. The explanation proposed for this relies on the well-known fact that the SCR of NO/NO<sub>2</sub> mixtures (Eq. (1)) is much faster than the SCR of NO alone (Eq. (2)).



It is therefore inferred that part or the NO is oxidized to NO<sub>2</sub> over the oxidation component, which opens fast SCR as a new reaction channel for the system. This is actually what happens in equipment for urea-SCR where Diesel oxidation catalysts upstream urea injection are upgraded in a way that they produce sufficient NO<sub>2</sub> from

\* Corresponding author at: Lehrstuhl für Technische Chemie, Ruhr-Universität Bochum, P. O. Box 102148, D-44780 Bochum, Germany. Fax: +49 234 321 4115.

E-mail address: [w.gruenert@techchem.ruhr-uni-bochum.de](mailto:w.gruenert@techchem.ruhr-uni-bochum.de) (W. Grünert).

<sup>1</sup> Present address: Oak Ridge National Laboratory, Knoxville, Tennessee, U. S. A.

the NO present, which allows the SCR catalyst to operate via fast SCR (Reaction (1)). In the hybrid catalysts, the oxidation component is no longer separated from the SCR catalyst, it faces the full reaction mixture including  $\text{NH}_3$ , which is easily oxidized as well.

In a study with a variety of oxidation components we have recently explored these synergies for a number of them when combined with Fe-ZSM-5 [4]. Huge activities and promising stabilities were observed with Mn-containing binary and ternary oxides. With Ce–Zr-oxide, synergistic effects were found as well, but the activity remained smaller. However, while  $\text{N}_2\text{O}$  and  $\text{NO}_2$  were formed in unacceptable extent at different reaction temperatures over Mn-containing systems, the hybrid with Ce–Zr-oxide was completely selective for  $\text{N}_2$ . Notably, an attempt to relate the observed synergistic effects to NO oxidation rates measured with the oxidation components resulted in a rather approximate correlation only while significant contradictions remained in detail. Therefore, the consecutive scheme of standard SCR proceeding via NO oxidation and fast SCR could not be unequivocally proven for the hybrid catalysts.

In mechanical mixtures, the spatial separation of components is a promising approach to study the functions of the components separately. Chemical stability of the molecule which carries the reaction from one component to the other one is an indispensable requirement for this approach. The stability of  $\text{NO}_2$  is evident from the success of the commercial scheme with  $\text{NO}_2$  formation (far) upstream of the SCR catalyst. The present paper communicates the result of studies devoted to confirm the applicability of this approach to our hybrid catalysts. Its failure suggests that  $\text{NO}_2$  may not be the mediating component. To enlarge the experimental basis for the discussion, the hybrid concept will be initially extended to the use of  $\text{V}_2\text{O}_5$ – $\text{WO}_3/\text{TiO}_2$  as the SCR component.

## 2. Experimental

### 2.1. Catalyst preparation

The preparation of most catalyst components has been described earlier [4]. Fe-ZSM-5 was made by solid-state ion exchange (for details see Ref. [5], for XRD of the sample—Ref. [4]), its Fe content was determined to be 0.4 wt.%. The second SCR component ( $\text{V}_2\text{O}_5$ – $\text{WO}_3/\text{TiO}_2$ , “V–W/Ti”) was prepared by impregnating a 10 wt.%  $\text{WO}_3/\text{TiO}_2$  support supplied by Huntsman Pigments and Additives with an aqueous solution of  $\text{NH}_4\text{VO}_3$  (0.356 g/L) at pH 9 to obtain 0.5 wt.% of  $\text{V}_2\text{O}_5$ . After drying at room temperature, the sample was aged in flowing air at 1023 K for 1 h. After this treatment, the BET surface area of the catalyst was 33  $\text{m}^2/\text{g}$ , its X-ray diffractogram (not shown) did not exhibit signals of V or W phases.

Oxidation components used were  $\text{Mn}_2\text{O}_3$ , hopcalite, and Ce–Zr $\text{O}_2$ .  $\text{Mn}_2\text{O}_3$  was made by precipitating Mn hydroxide from Mn acetate solution by adding aqueous ammonia up to pH 8. The precipitate was washed, dried and calcined in flowing air at 923 K for 2 h. The resulting solid was identified as  $\text{Mn}_2\text{O}_3$  by XRD, its BET surface area was determined to be 11  $\text{m}^2/\text{g}$ . Hopcalites are  $\text{MnO}_x$ – $\text{CuO}_x$  mixed oxides. The sample used in our work (“Mn–Cu”) was supplied by Cardiff University, its preparation and basic characterization is described in Ref. [6], for XRD and XPS data see Ref. [4]. The ceria–zirconia mixed oxide (“Ce–Zr”) was donated by Umicore AG & Co. KG.

For preparing the hybrid catalysts, oxidation and SCR components were mixed at a weight ratio 1/1 in four different ways (Fig. 1): as mixed particles (MP) by thoroughly grinding the components in a mortar and producing particles (250–350  $\mu\text{m}$ , 45–60 mesh) via the traditional route of pressing and sieving, as separate particles (SP) by making particles of the same size from the individually ground components and combining these

particles into a single catalyst bed, by arranging the SP into four consecutive beds of single components, the oxidation component always upstream of the SCR component (4L), and as a two-layer sequence of oxidation and SCR catalyst (2L).

### 2.2. Catalytic measurements

Catalytic data of standard SCR were measured in flow regime using a microflow quartz reactor (4.2 mm i.d.) inserted into an electric tubular furnace. Gas lines after and before the reactors were kept at 353 K to avoid water condensation, in case of fast SCR at 423 K to suppress formation of  $\text{NH}_4\text{NO}_3$ . Measurements were carried out at atmospheric pressure and temperatures between 373 and 873 K. The GHSV was adjusted to 300,000  $\text{h}^{-1}$  for the hybrid catalysts, while individual components were subjected to 600,000  $\text{h}^{-1}$  in order to identify their possible contribution to activity and selectivity in the hybrid systems. In these experiments, catalyst masses were 25 mg (hybrids) or 12.5 mg (components), while the feed consisted of 1000 ppm NO, 1000 ppm  $\text{NH}_3$ , 2 vol.%  $\text{O}_2$ , balanced with He (moisture was omitted in this studies as it was devoted to a mechanistic detail). In most cases, a second identical run was performed after the first one, which provides initial insight into the changes caused by exposure to high temperatures (peak temperature of first run—873 K). Such changes were expected in cases where oxidation components calcined at low temperatures (e.g., hopcalites) had been used, but they may generally arise from interactions between both components in particular in the MP arrangement. Studies of fast SCR were performed under the same conditions, with half of the NO in the feed (500 ppm) replaced by  $\text{NO}_2$  and a less extended temperature range (473–673 K) at 600,000  $\text{h}^{-1}$ .

In the steady state, NO,  $\text{NO}_2$  and  $\text{NH}_3$  concentrations were analyzed on-line using an XStream X2 Gas Analyzer (Rosemount Analytical; Emerson) which combines non-dispersive infrared and ultraviolet spectrometry for quantitative determination. Nitrous oxide ( $\text{N}_2\text{O}$ ) was determined with a ABB Advanced Optima Continuous Gas Analyzer (A02000 Series). Additional a quantification of  $\text{N}_2\text{O}$  and  $\text{N}_2$  took place by using a quadrupole mass spectrometer (Omnistar, Pfeiffer) calibrated by an internal standard. For the fast SCR measurements, a  $\text{NH}_3$ -trap which is inert toward the nitrogen oxides (Bühler) was inserted prior to the XStream to avoid ammonium nitrate formation in the cuvettes. In this case,  $\text{NH}_3$  conversion was evaluated from the mass-spectrometric data. Conversions were calculated according to:

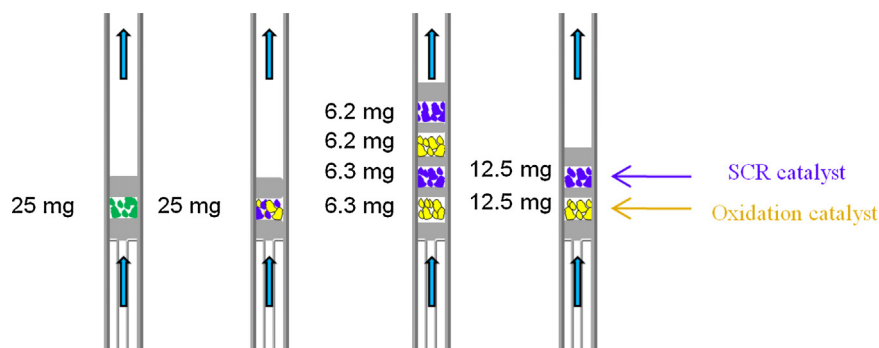
$$X_i(\%) = \frac{C_{i,\text{in}} - C_{i,\text{out}}}{C_{i,\text{in}}} \times 100\%$$

(i – NO or  $\text{NH}_3$ ). By-product formation will be reported by the concentrations of  $\text{N}_2\text{O}$  and  $\text{NO}_2$  obtained.

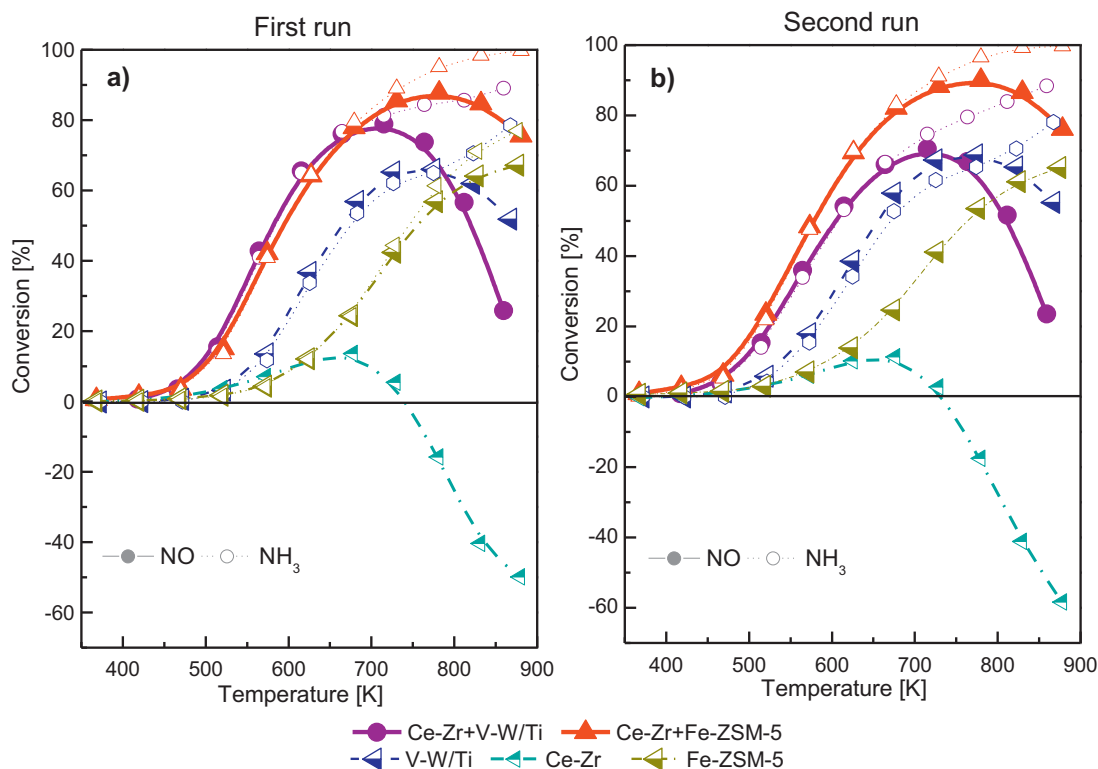
## 3. Results

### 3.1. Hybrids with $\text{V}_2\text{O}_5$ – $\text{WO}_3/\text{TiO}_2$

In Fig. 2a, NO conversions measured with hybrids composed of the Ce–Zr oxidation component and Fe-ZSM-5 or V–W/Ti are compared. The Ce–Zr@Fe-ZSM-5 hybrid was already described in our previous report [4], its data and those of its components have been cited from this paper. The NO conversion curve of the Ce–Zr@V–W/Ti hybrid is almost identical with that of the zeolite-containing one up to 700 K. Fig. 2a also presents the NO conversions measured with the V–W/Ti component alone, which is more active than the Fe-ZSM-5 employed in this study despite its exposure to high temperatures (see above). The extent of synergy is therefore smaller with the V–W/Ti component, but a closer look shows that it definitely exists up to 623 K. Above 700 K, NO conversion decreases strongly upon further moderate increase of  $\text{NH}_3$  conversion.



**Fig. 1.** Structure of catalyst beds: mixed particles (MP), separate particles (SP), four-layer arrangement (4L) and two-layer arrangement (2L), from left to right.



**Fig. 2.** Comparison of synergetic effects obtained with the Ce–ZrO<sub>x</sub> oxidation component with different SCR components—Fe–ZSM-5 and V<sub>2</sub>O<sub>3</sub>–WO<sub>3</sub>/TiO<sub>2</sub>, a, first run, b, second run directly consecutive to first run. For by-product formation see Fig. S-1 (Supporting information).

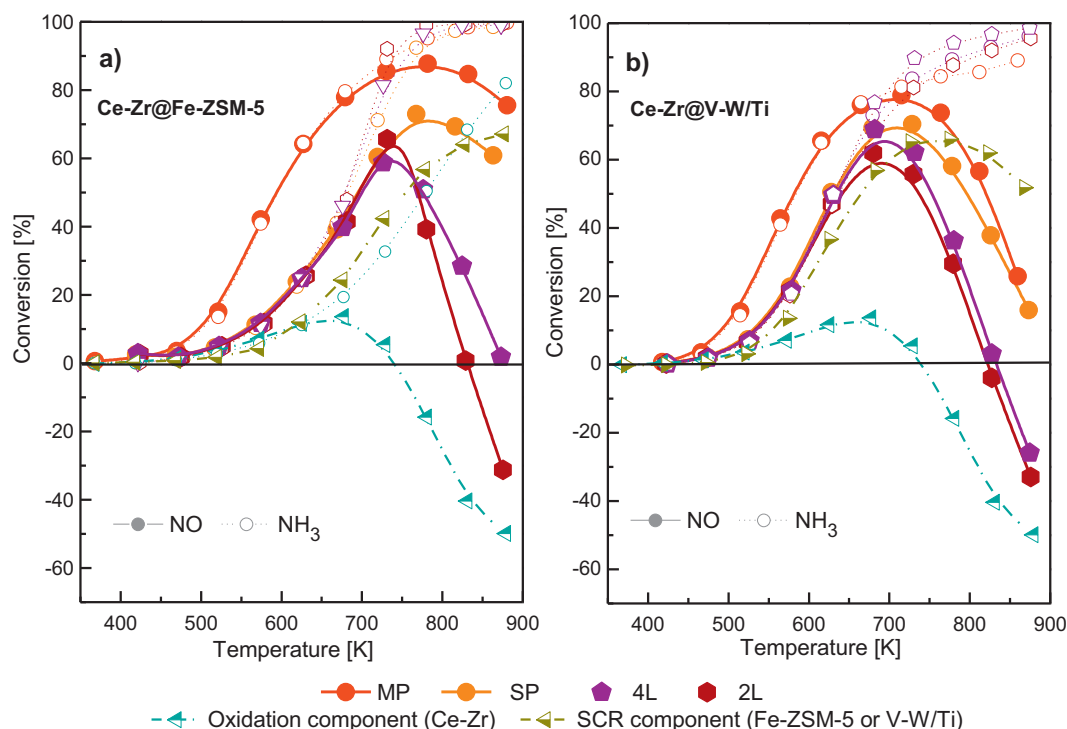
Analysis of the by-products (Fig. S1, Supporting information) shows that this happens without the concomitant formation of N<sub>2</sub>O usually observed with V<sub>2</sub>O<sub>5</sub>/TiO<sub>2</sub> catalysts (cf. data for V–W/Ti in Fig. S1a). This behavior is likely to originate from the Ce–Zr component, which catalyses NH<sub>3</sub> oxidation efficiently but with only moderate N<sub>2</sub>O formation under these conditions (Figs. 2a, S1a). It is, however, different from that of the zeolite-based hybrid, which achieves increasing NO conversions up to almost 800 K (Fig. 2a).

Fig. 2b reports the NO conversions obtained in the repetitive run, i.e., after exposure of the catalysts to 873 K. The Ce–Zr@Fe–ZSM-5 hybrid seems even more active now, although the significance of this observation needs to be supported by additional measurements. Opposed to this, the Ce–Zr@V–W/Ti hybrid is significantly deactivated and the synergetic effect has become smaller though still detectable. Similar observations have been made with hybrids in which V–W/Ti was combined with Mn-containing oxidation components [7]: here, weak synergies were obtained for the fresh catalysts as well, while the loss of performance in the second run was even more drastic than with the Ce–Zr oxidation component.

In Fig. S2, the performance of the two SCR components in fast SCR is compared, the data of Fe–ZSM-5 again originating from Ref. [4]. Obviously, V–W/Ti is much less active for fast SCR than Fe–ZSM-5. Still, the NO<sub>x</sub> conversions over the former are significantly larger than those obtained with the Ce–Zr@V–W/Ti hybrid in standard SCR (Fig. 2a). Therefore, NO oxidation over the Ce–Zr component should be rate limiting within the consecutive scheme, which is in agreement with the rather low NO oxidation activity of this catalyst [4]. Indeed, the NO conversions in standard SCR do not differ in a wide temperature range between two composites containing components with very different activities for fast SCR (Fig. 2a). It remains, however, unclear why the high-temperature behavior, which apparently originates from the Ce–Zr component as well, is so different in these two systems.

### 3.2. Experiments with structured beds

The effect of particle separation on the behavior of the hybrid systems discussed in Section 3.1 is shown in Fig. 3. In both cases,



**Fig. 3.** Influence of the particle separation on hybrid systems involving the Ce-ZrO<sub>x</sub> oxidation component, a, Ce-Zr@VW/Ti, b, Ce-Zr@Fe-ZSM-5. For by-product formation see Fig. S-3 (Supporting information).

the synergy largely collapses already after collecting the components in separate particles and mixing them. The loss is most pronounced in the zeolite-containing hybrid (Fig. 3a) because of its more intense synergistic effect. The SP, 4L, and 2L arrangements provide completely identical low-temperature NO conversions but differ strongly beyond 700 K. The separate-particle bed still achieves sizeable high-temperature NO conversions. In particular in the Ce-Zr@Fe-ZSM-5 system, this can be even considered as a synergy because the sum of NO conversions over Fe-ZSM-5 and Ce-Zr is clearly smaller than over the SP composite beyond 723 K. Opposed to this, the arrangement of the components in separate layers results in intense NH<sub>3</sub> oxidation by the Ce-Zr component in both hybrids. The most segregated structure (2L) causes the most drastic ammonia oxidation. This is more significant in the zeolite-based composite (Fig. 3a), but as the conversion curves of the 2L and the 4L experiments are completely identical also over the V-based version (Fig. 3b), the moderate differences between them in the high-temperature range can probably be considered significant.

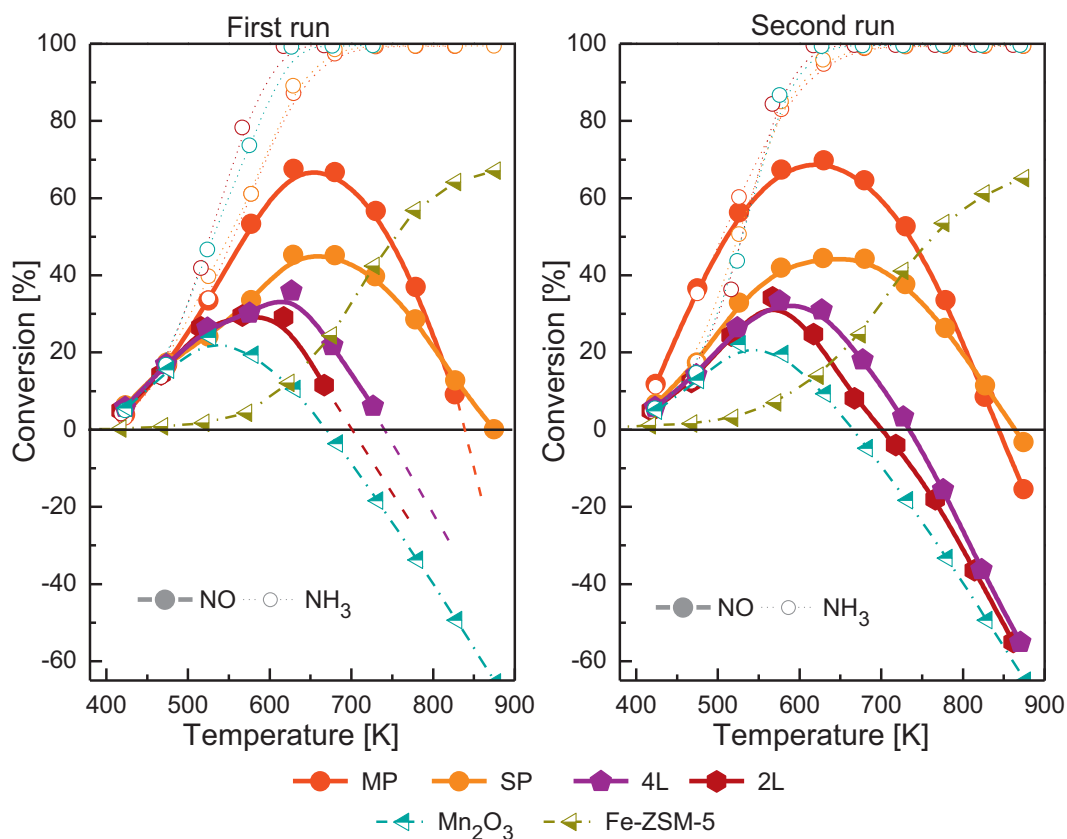
The by-product formation in these systems is summarized in Fig. S3. It is very low in the zeolite-containing hybrid (Fig. S3a, b). Remarkably, Fe-ZSM-5 suppressed the tendency of Ce-Zr to release N<sub>2</sub>O and in particular NO<sub>2</sub> at higher temperatures even in the more segregated bed arrangements. Opposed to this, the SCR component V-W/Ti is prone to N<sub>2</sub>O formation at higher temperatures itself. In the well-mixed hybrids, this tendency is significantly decreased. In case of NO<sub>2</sub> formation, unequivocal trends could not be observed.

Figs. 4, 5, S4 and S5 summarize analogous studies with Mn-containing oxidation catalysts, where significant changes were observed upon repeating the experiment (2nd run). Surprisingly, such change occurred even with Mn<sub>2</sub>O<sub>3</sub> (Figs. 4 and S4) which had been subjected to 923 K during preparation. The trends of NO and NH<sub>3</sub> conversions in the first run (Fig. 4a) comply well with the previous cases: intimate mixing (MP) resulted in a strong synergy, which decreased and disappeared upon separation of the hybrid components. A significant synergy could be detected also in the SP arrangement: already above 573 K, the NO conversions over this

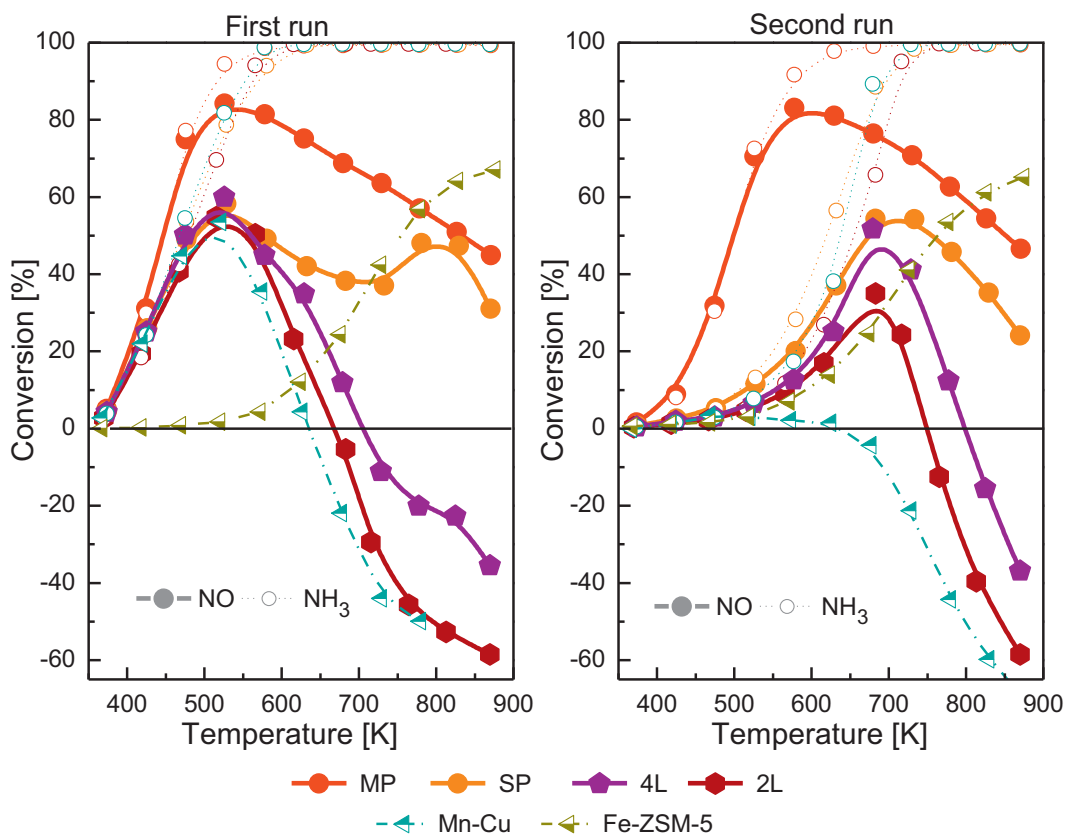
bed were clearly larger than the sum of conversions over Mn<sub>2</sub>O<sub>3</sub> and Fe-ZSM-5. They remained positive in the whole temperature range while those over Mn<sub>2</sub>O<sub>3</sub> and the 4L and 2L beds became strongly negative at high temperatures (due to an experimental flaw, this has not been recorded in the latter cases, it has been indicated by analogy to the 2nd run). In the second run, the activity of the MP bed increased substantially: the temperature of 50% NO conversion (light-off,  $T_{50}$ ) decreased by as much as 60 K. This applies, however, only to the low-temperature region while the behavior remained the same at high temperatures. Analogously, some change at low temperatures can be seen in the SP case, but its significance is not beyond doubt. The high-temperature region remained unchanged. We took this to justify the reconstruction of high-temperature trends of the 4L and 2L experiments in Fig. 4a because the conversion curves of both runs were identical already at low temperatures.

The influence of component separation on the synergistic effect can be also detected in the release of by-products, which is very intense with Mn<sub>2</sub>O<sub>3</sub> both for N<sub>2</sub>O and NO<sub>2</sub> (Fig. S4). Over the well-mixed bed (MP), this release was substantially though not completely suppressed (Fig. S4a). Some of this synergy was kept by the SP bed while the 4L and in particular the 2L beds behaved like the pure Mn<sub>2</sub>O<sub>3</sub>. The enhanced activity of the MP and possibly SP beds in the second run was not reflected in by-product formation (Fig. S4b), but surprisingly, the N<sub>2</sub>O formation over the 2L bed became slightly lower and indistinguishable from that over the 4L bed.

Figs. 5 and S5 report what happens with the spectacular synergies observed upon combination of Fe-ZSM-5 with hopcalite [4]. The decrease of synergy with increasing distance between the components is the same as before. Again, a clear synergy can be observed at high temperatures also for SP. Here, NO conversion even exhibits a second peak around 800 K. A shoulder in the 4L curve in the same temperature range shows that this result is not spurious. The NO conversion curve of the 4L arrangement follows closely that of the pure Mn<sub>2</sub>O<sub>3</sub>. Above a conversion peak at 523 K,



**Fig. 4.** Influence of the particle separation on the hybrid system composed of  $\text{Mn}_2\text{O}_3$  and Fe-ZSM-5, a, first run, b, second run directly consecutive to first run. For by-product formation see Fig. S-4 (Supporting information).



**Fig. 5.** Influence of the particle separation on the hybrid system composed of Mn–Cu mixed oxide (hopcalite) and Fe-ZSM-5, a, first run, b, second run directly consecutive to first run. For by-product formation see Fig. S-5 (Supporting information).



both curves decrease sharply, that of the 4 L bed remaining 15–20% above that of  $\text{Mn}_2\text{O}_3$ . This is certainly an effect of the following Fe-ZSM-5 bed, but it cannot be related to the SCR activity of the zeolite.

The maintenance of the synergy despite a very effective deactivation of the hopcalite component, which was the most unexpected result in our earlier work on hybrid catalysts [4], has been confirmed in the present study. While  $T_{50}$  increased by ca. 50%, an intense synergy is still obvious although the collapsed hopcalite alone (for structural information see [4]) converted hardly any NO and reacted even ammonia to less than 10% up to 523 K (where the MP bed achieves 80% NO conversion). The breakdown of synergy with increasing particle separation was most drastic in this mixture, but again, there was some synergy with the SP bed and maybe even with the 4 L arrangement. Similar to the Ce-Zr-based composites (Fig. 3), NO conversion paralleled that of Fe-ZSM-5 up to a conversion peak, beyond which it decreased, most steeply over the layered arrangements.

The intense by-product formation precludes the hopcalite@Fe-ZSM-5 system from any commercial potential. Over the MP bed, the release of  $\text{N}_2\text{O}$  was somewhat decreased relative to the pure hopcalite, but it returned to almost its original level already with the SP arrangement (Figs. S5a,b).  $\text{NO}_2$  formation was slightly suppressed vs. the pure hopcalite in the MP and SP arrangements. The thermally degraded hopcalite was almost inactive for  $\text{N}_2\text{O}$  formation but released  $\text{NO}_2$  in similar quantities as the initial one (Figs. S5c,d). While the latter is decreased to some extent—and even more than with the fresh hopcalite—by the admixture of Fe-ZSM-5, a remarkable observation related to  $\text{N}_2\text{O}$ , which was made already in [4], was reproduced and supported here: the release of  $\text{N}_2\text{O}$  was significantly more intense over the well-mixed hybrid than over the pure oxidation component (degraded hopcalite), which is the opposite of the usual trends. A slight maximum of  $\text{N}_2\text{O}$  formation occurred also with the SP bed, only the layered arrangements behaved like the pure oxidation component.

#### 4. Discussion

The results presented here clearly show that the synergistic effects observed do not operate via the formation of  $\text{NO}_2$ . Nitrogen dioxide is a stable molecule which could easily travel between different particles of a bed or from its origin to a downstream place of consumption as it does in commercial urea-SCR facilities. This raises a number of questions: What else mediates the interaction between the hybrid components? Why is  $\text{NO}_2$  not formed although the oxidation components, in particular those containing Mn, are highly active for NO oxidation [4]?

The breakdown of the synergy upon separation of the hybrid components may indicate two possible interaction mechanisms: parts of the reaction mechanism proceeding on the different components may be linked by a short-lived intermediate or the new active sites may have been formed by solid-state reactions. The latter, although probably occurring to a limited extent at high temperatures, is unlikely to cause the spectacular gains in activity. The most likely type of solid-state reaction in these systems is solid-state ion exchange. With  $\text{Mn}_2\text{O}_3$ , this would result in intra-zeolite Mn cations, which have been found to be very inactive in standard SCR [7]. In the case of hopcalite, the zeolite could become doped with highly active Cu ions. Intra-zeolite Cu ions can easily be identified by combining XPS and X-ray induced Auger spectroscopy, but our recent effort to detect them in a Mn-Cu@Fe-ZSM-5 hybrid calcined at high temperature failed [4].

The reaction mechanism of standard SCR over Cu and Fe zeolites has recently been subject of a controversy. A popular mechanism according to which these catalysts operate via a sequence of NO

oxidation and fast SCR (2) [8], similar as proposed for the hybrids in literature [3], has been challenged by E. Tronconi's and our groups based on different pieces of evidence [9–12]. In a trapping study with  $\text{BaO}/\text{Al}_2\text{O}_3$ , Ruggeri et al. demonstrated that gaseous  $\text{HNO}_2$  is formed during NO oxidation over Fe-ZSM-5 [12,13]. In agreement with earlier suggestions of Sun et al. [14], Ruggeri et al. consider it to be the crucial intermediate, which forms the highly unstable  $\text{NH}_4\text{NO}_2$  with adsorbed ammonia. This might be a promising alternative also for the hybrid system:  $\text{HNO}_2$  might be formed as an intermediate of NO oxidation over the oxidation component and would further be converted with  $\text{NH}_3$  to  $\text{N}_2$  and water after making the way (in) to the SCR component.

Another labile intermediate, which has been used to explain synergistic effects in other circumstances, is  $\text{N}_2\text{O}_4$  [15]. As it is unlikely that this  $\text{NO}_2$  dimer could be obtained directly by NO oxidation over the oxidation component, it could be formed only from  $\text{NO}_2$ . For reasons of equilibrium, the latter would have to be present in excess at the relevant temperatures and would be free to react via the fast SCR path, which is just the situation we exclude by our study. We therefore consider  $\text{N}_2\text{O}_4$  an unlikely option.

While a possible mediating role of  $\text{HNO}_2$  will have to be substantiated by more experimental work, it may be able to explain several observations. As  $\text{HNO}_2$  is considered to be an intermediate of  $\text{NO}_2$  formation, it is plausible that the synergistic effects are related to but not scaling with the NO oxidation activity. Deviations from the correlation may be due to different behaviors of the oxidation components with respect to later steps in the NO oxidation mechanism. Different NO oxidation activities may also explain why the Mn-based hybrids provide a synergistic effect already at lower temperatures than the Ce-Zr@Fe-ZSM-5 catalyst. Notably, this suggestion provides also a first approach to understand the surprising observation that the degraded hopcalite (essentially a  $(\text{CuMn})_3\text{O}_4$  spinel [4]) causes drastic synergies when mixed with Fe-ZSM-5 at temperatures where it does not catalyze oxidation neither of NO nor  $\text{NH}_3$  to any significant extent (Fig. 5b). Apparently, the required intermediate ( $\text{HNO}_2$ ?) is formed on this component. It finds the zeolite to react at the sites therein, while its further reaction on the  $\text{CuMnO}_x$  surface to  $\text{NO}_2$  seems to be hindered.

On the other hand, this reasoning shows that the reaction mechanism of NO oxidation must be completely reversible at least until the (unstable) intermediate mediating the process. The reaction of the latter with gas-phase  $\text{NH}_3$ , which is always available during standard SCR, seems to be too slow to result in a parallel reaction channel to  $\text{N}_2$  and  $\text{H}_2\text{O}$ : when the intermediate does not find the sites of the SCR component it decays into the reactants, and the conversion remains small (or will be determined by the Fe-ZSM-5 present as shown in Figs. 5b and 3a).

The sometimes drastic differences between MP and SP (or layered) hybrids (see for instance Figs. 3a, 4b, 5b) indicate another feature of the link between formation and consumption of the reactive intermediate. One should think that the chemistry on the surface of the oxidation catalyst should not strongly depend on the structure of the mechanical mixture, and yet, the presence of the zeolite nearby causes major changes in conversion. The SCR component (in particular the zeolite based one) appears to present a very effective potential sink for desorption and diffusion of the intermediate, much more than the mere gas phase which seems to delay the surface reactions. This may have physical reasons: it is known that mass transfer over a phase boundary can be strongly accelerated when the diffusing molecule is reacted in the target phase. This acceleration can be quantified by enhancement factors, which can be related to engineering parameters like the Hatta number [16]. The trapping experiment of Ruggeri et al. [13] seems to contain a similar feature: embedding Fe-ZSM-5, which is the  $\text{HNO}_2$  source here, into the trapping  $\text{BaO}/\text{Al}_2\text{O}_3$  material caused a long delay of  $\text{NO}_2$  formation while the species detected on the BaO were almost

exclusively nitrites. Apparently, the drain of the trapping component successfully competed for the  $\text{HNO}_2$  intermediate with the subsequent steps of  $\text{NO}_2$  formation in this transient period.

The failure to utilize  $\text{NO}_2$  for the synergy is certainly due to the presence of  $\text{NH}_3$ . In the layered structures, NO conversion over the hybrids follows those over the frontend oxidation component, which is too busy with SCR to form  $\text{NO}_2$ . Just some increment is added by the SCR component. At higher temperatures, the oxidation catalyst predominantly oxidizes  $\text{NH}_3$  and causes negative conversions, which are again slightly modified by the redox activity of Fe-ZSM-5. The remarkable point is that the presence of Fe-ZSM-5 precludes even this path to a significant extent, maybe by drainage of a reactive intermediate like  $\text{HNO}_2$ . This enables a further selective conversion of this intermediate, which at the same time removes  $\text{NH}_3$  from the feed saving it from total oxidation.

## 5. Conclusions

The performance of hybrid catalysts for the SCR of NO by  $\text{NH}_3$  consisting of physical mixtures of an oxidation component ( $\text{Mn}_2\text{O}_3$ , hopcalite, Ce-ZrO<sub>x</sub>) with an SCR component (Fe-ZSM-5,  $\text{V}_2\text{O}_5\text{-WO}_3/\text{TiO}_2$ ) strongly depends on the separation between the components. The drastic synergies described in literature are observed only when the components are thoroughly mixed and pressed into mixed particles. The synergy is strongly though not completely suppressed when particles containing the individual components are mixed, but breaks down when the system is arranged in individual layers. This observation is at variance with views according to which  $\text{NO}_2$  mediates the cooperation between the oxidation and the SCR component because this molecule could easily travel over the distances involved. On the basis of recent literature, it is proposed that this function may be fulfilled by a more labile intermediate, e.g.,  $\text{HNO}_2$ .

This might explain earlier observations that the correlation between NO oxidation activities of oxidation components and the performance of the resulting hybrid was observed to be coarse, to contain remarkable outliers, and to involve even an example of a system working well with a component apparently inactive for NO oxidation (deactivated hopcalite). The sometimes drastic differences between completely mixed and more segregated systems is further ascribed to enhanced diffusion rates of the critical intermediate in the fully mixed system, where the zeolite offers a nearby sink for the molecule, which is missing in more segregated systems.

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## Appendix A. Supplementary data

Supplementary data associated with this article can be found, in the online version, at <http://dx.doi.org/10.1016/j.apcatb.2015.09.028>.

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